Ordered Pillar Array Structures of TiO_2 by Nanoimprinting Using Anodic Porous Alumina as Molds

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Ordered pillar array structures of TiO_2 were prepared by nanoimprinting process using ordered anodic porous alumina as a mold. The shape of the obtained pillars of TiO_2 corresponded to that of the holes of anodic porous alumina used as a mold. The geometric structure of the TiO_2 pillar array could be controlled by the condition of the formation of the anodic porous alumina molds.

There have been growing interests in the nanoimprinting process, in which fine patterns are formed using a mold in contact with substrates, because of their capability of high throughput formation of fine patterns on a submicron to nanometer scale.[1–3] Currently, the nanoimprinting process is extensively applied to the molding of various kinds of polymers. In contrast to this, application of nanoimprinting to inorganic materials is restricted.[4,5] As an example of nanoimprinting for inorganic materials, formation of fine patterns of SiO_2 using sip-on glass have been reported. In the present report, we show the formation of ordered fine structures of TiO_2 by nanoimprinting using anodic porous alumina as a mold for the first time. TiO_2 is a key material for the preparation of functional optical devices, such as photocatalysts or solar cells.[6,7] To optimize the performance of the obtained devices, control of the geometric structures of TiO_2 from micron to nanometer scale is essential. Application of nanoimprinting, which allows the repeated use of a mold, will contribute to the high throughput formation of functional devices. In the present work, anodic porous alumina, which is formed by anodization of Al in acidic solution, was used as a mold.[8–11] Application of ordered unique geometric structures of anodic porous alumina to the mold for nanoimprinting enables the formation of fine TiO_2 structures with high aspect features in addition to large sample area.

Figure 1 shows the schematic for the preparation of ordered structures of TiO_2 pillars. Anodic porous alumina molds with ideally ordered hole arrangement was prepared by a process similar to that reported previously.[12] The hole period in the anodic porous alumina was 500 nm. In the present experiment, the shape of the holes of the porous alumina was figured to be tapered by a combination process composed of the repetition of the anodization and etching to facilitate the release of the mold from the imprinted layer.[13] The first anodization was carried out in 0.1 M phosphoric acid under the constant anodization voltage of 200 V at 0 °C. Then the sample was dipped in 10 wt % phosphoric acid at 30 °C for 25 min. The five times repetition of these processes generated anodic porous alumina with tapered holes. The depth of the holes was adjusted by the time of each anodization.

Ordered pillar array structures of TiO_2 were fabricated by nanoimprinting using TiO_2 paste (18NR, Catalysts and Chemicals Ind), which contained TiO_2 small particles of 20 nm in diameter. The crystal form of the particles was anatase. Prior to the nanoimprinting, the anodic porous alumina mold were treated with a fluoroalkylsilane solution (Optool DSX, Daikin Industries Ldt.) to form the releasing layer. The TiO_2 paste was fed into the anodic porous alumina mold and was heated at 200 °C for 1 h. The ordered pillar array structure of TiO_2 was obtained by detaching the solidified TiO_2 layer from the mold using an adhesion tape. The obtained samples were observed using a scanning electron microscope (SEM: JSM-6700F, JEOL).

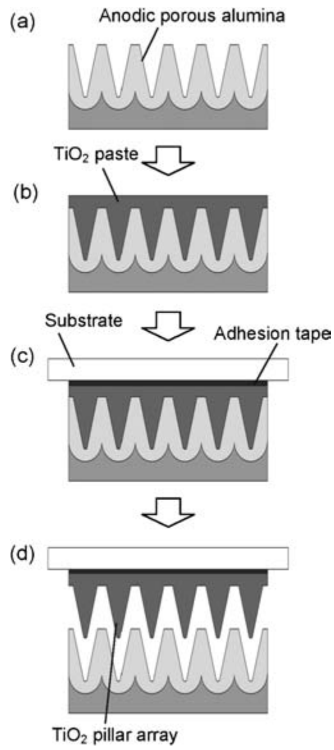

Figure 1. Schematic of fabrication process of TiO_2 nanopillar array: (a) anodic porous alumina mold with tapered holes, (b) filling of TiO_2 paste into alumina holes and heat treatment, (c) adhesion of substrate, (d) detachment of mold.

Figure 2 shows the cross-sectional SEM image of the anodic porous alumina used as a mold for nanoimprinting. For this sample, time for each anodization was 30 s. From Figure 2, ordered hole array structure can be observed. In the case of the sample in Figure 2, the hole interval, hole size at opening, and hole depth were 500, 280, and 130 nm, respectively.

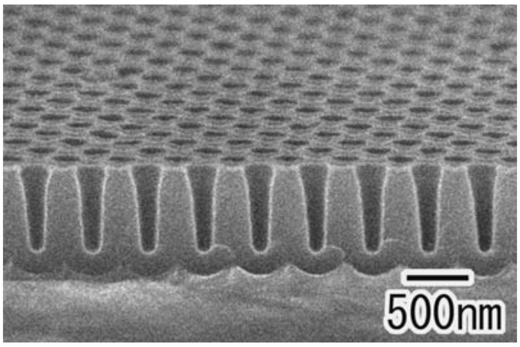

Figure 2. SEM image of anodic porous alumina mold.

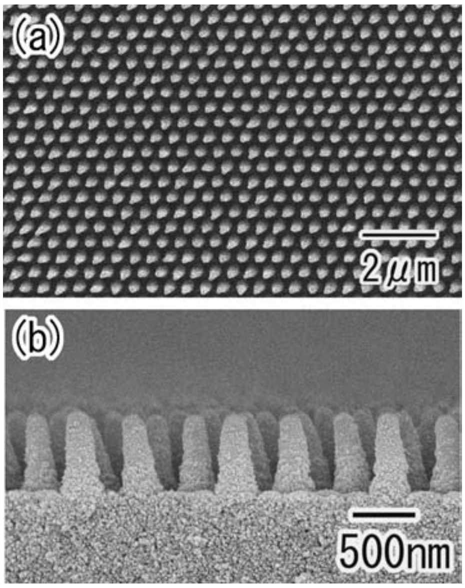

Figure 3. SEM images of TiO_2 pillar array: (a) surface and (b) cross-sectional view.

Figure 3 shows the SEM images of the obtained TiO_2 pillar array formed by nanoimprinting. After the imprinting, the sample was heat-treated at 200 °C for 1 h for the solidification. From the surface SEM image in Figure 3a, it can be confirmed that TiO_2 pillars are arranged orderly over the sample. From the cross-sectional image in Figure 3b, TiO_2 pillars stand upright on the substrate. The diameter and the height of each pillar are somewhat smaller than those of the holes in the anodic porous alumina used as a mold. This is due to the shrinkage of the TiO_2 pillars during the heat treatment. The use of the releasing agent on the mold made it easy to detach the mold from the TiO_2 and allowed the repeated use of the mold.

One advantageous points of the use of anodic porous alumina as a mold is the capability of formation of structures with high aspect ratios. Figure 4 shows the cross-sectional SEM image of a TiO_2 pillar array prepared by the imprinting using a mold with deeper holes. For this sample, an anodic porous alumina mold with deeper holes was needed. The time for each anodization was 45 s. From Figure 4, it is observed that TiO_2 pillars with higher aspect ratio can be held upright on the substrate. In the case of the sample in Figure 4, the height of the pillars is 1.4 μm that corresponds to the aspect ratio of 7.

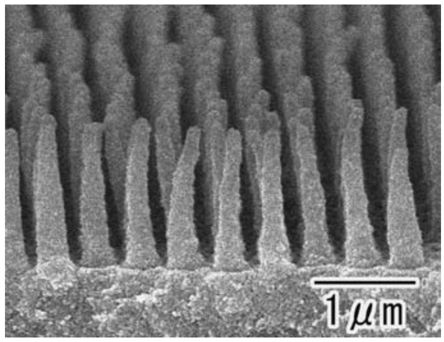

Figure 4. SEM image of TiO_2 pillar array with high aspect ratio.

In conclusion, the ordered pillar arrays of TiO_2 could be formed by nanoimprinting using anodic porous alumina as a mold. The geometric structures of the obtained TiO_2 pillar array could be controlled by the conditions of formation of anodic porous alumina used for the nanoimprinting. The pillar array structures of TiO_2 obtained by the present process will be used for the preparation of various types of functional optical devices. In addition to this, the TiO_2 pillar array will be used for antireflection structures for the substrate with high refractive indexes.

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